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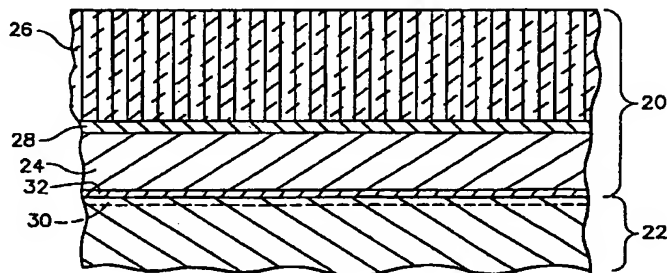
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(54) **Bond coat for a thermal barrier coating system**

(57) A thermal barrier coating system (20) for the surface of an article (22) designed for use in a hostile thermal environment, such as turbine, combustor and augmentor components of a gas turbine engine. The thermal barrier coating system (20) employs a bond coat (24) of a nickel aluminide alloy over which a thermal-insulating ceramic layer (26) is deposited. The nickel aluminide bond coat (24) contains zirconium, but is otherwise predominantly of the beta ( $\beta$ ) NiAl phase. The bond coat (24) is preferably deposited by a physical

vapor deposition process (PVD), such as by magnetron sputtering, electron beam physical vapor deposition (EBPVD), jet vapor deposition (JVD) and plasma spray. The NiAl bond coat (24) with zirconium additions of between 0.05 and 0.5 atomic percent have been shown to exhibit drastically improved thermal fatigue life over prior art bond coats, with optimal results appearing to be obtained at or near 0.1 atomic percent zirconium.



**FIG. 2**

## Description

[0001] This invention relates to a bond coat for thermal barrier coating systems of the type used to protect components exposed to high temperature environments, such as the hostile thermal environment of a gas turbine engine. More particularly, this invention is directed to a thermal barrier coating system that includes a binary NiAl bond coat deposited by a physical vapor deposition technique and on which a thermal insulating ceramic layer is deposited, wherein the thermal life of the coating system is greatly enhanced by very limited additions of zirconium to the bond coat material.

[0002] Higher operating temperatures for gas turbine engines are continuously sought in order to increase their efficiency. However, as operating temperatures increase, the high temperature durability of the components of the engine must correspondingly increase. Significant advances in high temperature capabilities have been achieved through formulation of iron, nickel and cobalt-base superalloys, though such alloys alone are often inadequate to form components located in certain sections of a gas turbine engine, such as the turbine, combustor and augmentor. A common solution is to thermally insulate such components in order to minimize their service temperatures. For this purpose, thermal barrier coatings (TBC) formed on the exposed surfaces of high temperature components have found wide use.

[0003] To be effective, thermal barrier coatings must have low thermal conductivity, strongly adhere to the article, and remain adherent throughout many heating and cooling cycles. The latter requirement is particularly demanding due to the different coefficients of thermal expansion between materials having low thermal conductivity and superalloy materials typically used to form turbine engine components. Thermal barrier coating systems capable of satisfying the above requirements have generally required a metallic bond coat deposited on the component surface, followed by an adherent ceramic layer that serves to thermally insulate the component. Metal oxides, such as zirconia ( $ZrO_2$ ) that is partially or fully stabilized by yttria ( $Y_2O_3$ ), magnesia ( $MgO$ ) or other oxides, have been widely employed as the material for the thermal-insulating ceramic layer. The ceramic layer is typically deposited by air plasma spraying (APS), low pressure plasma spraying (LPPS), or a physical vapor deposition (PVD) technique, such as electron beam physical vapor deposition (EBPVD) which yields a strain-tolerant columnar grain structure. Bond coats are typically formed of an oxidation-resistant aluminum-based intermetallic such as a diffusion aluminide or platinum aluminide, or an oxidation-resistant aluminum-containing alloy such as MCrAlY (where M is iron, cobalt and/or nickel).

[0004] The aluminum content of the above-noted bond coat materials provides for the slow growth of a strong adherent continuous aluminum oxide layer (alumina scale) at elevated temperatures. This thermally grown oxide (TGO) protects the bond coat from oxidation and hot corrosion, and chemically bonds the ceramic layer to the bond coat. Though bond coat materials are particularly alloyed to be oxidation-resistant, the oxidation that occurs over time at elevated temperatures gradually depletes aluminum from the bond coat. Eventually, the level of aluminum within the bond coat is sufficiently depleted to prevent further slow growth of the protective oxide, and to allow for the more rapid growth of nonprotective oxides. At such time, spallation may occur at the interface between the bond coat and the aluminum oxide layer or the interface between the oxide layer and the ceramic layer.

[0005] In addition to depletion of aluminum, the ability of the bond coat to form the desired aluminum oxide layer can be hampered by the interdiffusion of elements between the superalloy and bond coat, such as during formation of a diffusion aluminide coating and during high temperature exposure. In particular, elements such as nickel, cobalt, chromium, titanium, tantalum, tungsten and molybdenum can increase the growth rate of aluminum oxide and form voluminous, nonadherent oxides or oxide scales that may be deleterious to the adhesion of the ceramic layer.

[0006] From the above, it is apparent that the service life of a thermal barrier coating is dependent on the bond coat used to anchor the thermal insulating ceramic layer. Once spallation of the ceramic layer has occurred, the component must be scrapped or refurbished at considerable cost by removing the remaining ceramic layer and bond coat, including any diffusion zone between the bond coat and substrate. Because removal of the diffusion zone effectively removes a portion of the substrate surface, a limited number of repairs can be performed before the component must be scrapped. In view of the considerable cost to repair and replace thermal barrier coating systems, there has been a considerable and continuous effort to increase their service life by improving the spallation resistance of the thermal insulating layer. However, such efforts have been complicated by the demand for higher service temperatures for gas turbine engines.

[0007] The present invention provides a thermal barrier coating on an article designed for use in a hostile thermal environment, such as turbine, combustor and augmentor components of a gas turbine engine. The invention is particularly directed to increasing the spallation resistance of a thermal barrier coating system with a bond coat that exhibits significantly improved oxidation resistance.

[0008] The thermal barrier coating system of this invention employs a bond coat of a nickel aluminide alloy over which a thermal-insulating ceramic layer is deposited, with the bond coat serving the traditional role of promoting adhesion of the ceramic layer to the article. According to the invention, the nickel aluminide bond coat contains zirconium and/or other reactive elements such as hafnium, yttrium and cesium, but is otherwise predominantly of the beta ( $\beta$ ) NiAl phase. As with prior art aluminum-containing bond coats, the bond coat of this invention develops a continuous aluminum oxide layer that promotes the adhesion of the ceramic layer to the bond coat. The bond coat is deposited by a physical vapor

deposition process (PVD), such as by magnetron sputtering, electron beam physical vapor deposition (EBPVD) and jet vapor deposition (JVD), though other deposition processes such as vacuum plasma spray (VPS), low pressure plasma spray (LPPS) and air plasma spray (APS) deposition are possible. The ceramic layer can be deposited on the bond coat by known techniques, including plasma spraying and PVD techniques. An aluminum oxide layer is preferably grown on the bond coat, either by heat treatment prior to deposition of the bond coat or during deposition of the ceramic layer.

**[0009]** A key feature of this invention is that the bond coat is not a traditional diffusion aluminide or MCrAlY coatings, but instead is a binary NiAl alloy consisting essentially of nickel and aluminum in stoichiometric amounts and containing zirconium in a very limited amount that has been unexpectedly found to drastically increase the service life of the thermal barrier coating system. In particular, zirconium additions of between 0.05 and 0.5 atomic percent have been shown to improve the life of a thermal barrier coating system by a factor of about two to in excess of ten when subjected to thermal cycle testing, with the best results appearing to be obtained at or near 0.1 atomic percent zirconium. The sensitivity that thermal life has for the zirconium content of the NiAl bond coat is particularly evident with increasing test temperatures, indicating that the bond coat of this invention is particularly advantageous for more demanding applications. It is believed that other reactive elements, such as hafnium, yttrium and cesium, would have a similar effect on a NiAl bond coat.

**[0010]** Another important aspect of the invention is that the bond coat is deposited in such a manner as to minimize diffusion of the bond coat constituents into the surface of the article. For example, a diffusion zone of not more than five micrometers is preferably achieved by the preferred PVD techniques. This reduced level of interaction between the bond coat and substrate promotes the formation of an initial layer of essentially pure aluminum oxide, promotes the slow growth of the protective aluminum oxide layer during service, and reduces the formation of voluminous nonadherent oxides of substrate constituents that tend to diffuse into the bond coat. Importantly, by limiting diffusion of the bond coat into the substrate, minimal substrate material must be removed during refurbishment of the thermal barrier coating system, when both the bond coat and thermal-insulating ceramic layer must be removed to allow deposition of a new bond coat and ceramic layer on the substrate.

**[0011]** Other objects and advantages of this invention will be better appreciated from the following detailed description with reference to the accompanying drawings, in which:-

Figure 1 is a perspective view of a high pressure turbine blade; and

Figure 2 is a cross-sectional view of the blade of Figure 1 along line 2-2, and shows a thermal barrier coating system on the blade in accordance with this invention.

**[0012]** The present invention is generally applicable to components that operate within environments characterized by relatively high temperatures, and are therefore subjected to severe thermal stresses and thermal cycling. Notable examples of such components include the high and low pressure turbine nozzles and blades, shrouds, combustor liners and augmentor hardware of gas turbine engines. One such example is the high pressure turbine blade 10 shown in Figure 1. The blade 10 generally includes an airfoil 12 against which hot combustion gases are directed during operation of the gas turbine engine, and whose surface is therefore subjected to severe attack by oxidation, corrosion and erosion. The airfoil 12 is anchored to a turbine disk (not shown) with a dovetail 14 formed on a root section 16 of the blade 10. Cooling passages 18 are present in the airfoil 12 through which bleed air is forced to transfer heat from the blade 10. While the advantages of this invention will be described with reference to the high pressure turbine blade 10 shown in Figure 1, the teachings of this invention are generally applicable to any component on which a thermal barrier coating system may be used to protect the component from its environment.

**[0013]** Represented in Figure 2 is a thermal barrier coating system 20 in accordance with this invention. As shown, the coating system 20 includes a ceramic layer 26 bonded to the blade substrate 22 with a bond coat 24. The substrate 22 (blade 10) is preferably a high-temperature material, such as an iron, nickel or cobalt-base superalloy. To attain a strain-tolerant columnar grain structure, the ceramic layer 26 is preferably deposited by physical vapor deposition (PVD), though other deposition techniques could be used. A preferred material for the ceramic layer 26 is an yttria-stabilized zirconia (YSZ), with a preferred composition being about 6 to about 8 weight percent yttria, though other ceramic materials could be used, such as yttria, nonstabilized zirconia, or zirconia stabilized by ceria ( $\text{CeO}_2$ ), scandia ( $\text{Sc}_2\text{O}_3$ ) or other oxides. The ceramic layer 26 is deposited to a thickness that is sufficient to provide the required thermal protection for the underlying substrate 22 and blade 10, generally on the order of about 125 to about 300 micrometers. As with prior art thermal barrier coating systems, the surface of the bond coat 24 oxidizes to form an aluminum oxide layer 28 to which the ceramic layer 26 chemically bonds.

**[0014]** According to the invention, the bond coat 24 is a nickel aluminide alloy of predominantly the beta ( $\beta$ ) NiAl phase with a very limited addition of zirconium. The NiAl bond coat 24 is formed using a PVD process, preferably sputtering, electron beam physical vapor deposition (EBPVD) or jet vapor deposition (JVD), though it is foreseeable that other deposition techniques could be used, such as plasma spraying. According to the invention, an adequate thickness for the NiAl bond coat 24 is about fifty micrometers in order to protect the underlying substrate 22 and provide an adequate

supply of aluminum for oxide formation, though thicknesses of about 25 to about 125 micrometers are believed to be suitable.

[0015] The preferred PVD techniques are preferably carried out to reduce the diffusion of the bond coat 24 into the substrate 22. Preferably, deposition of the bond coat 24 results in virtually no diffusion between the bond coat 24 and substrate 22. During subsequent heat treatment to relieve residual stresses generated during the deposition process, a very thin diffusion zone 30 of not more than above five micrometers, typically about 2.5 to 5 micrometers, may develop. A preferred heat treatment is conducted at about 1800°F (about 980°C) for about two to four hours in an inert atmosphere, such as argon. Importantly, the minimal thickness of the diffusion zone 30 promotes the initial formation of the oxide layer 28 as essentially pure aluminum oxide, promotes the slow growth of the protective aluminum oxide layer 28 during service, reduces the formation of voluminous nonadherent oxides at the bond coat-ceramic layer interface, and reduces the amount of substrate material that must be removed during refurbishment of the thermal barrier coating system 20. Accordingly, articles such as the blade 10 shown in Figure 1 can be refurbished more times than would be possible if a traditional bond coat were used.

[0016] As shown in Figure 2, an optional diffusion barrier layer 32 between the NiAl bond coat 24 and substrate 22 may be included to further inhibit interdiffusion and thereby improve the service life of the coating system 20. As noted above, it is believed that the initial aluminum oxide formed by the NiAl bond coat 24 provides the ground work for a slow growing oxide scale (thermally grown oxide; TGO). However, with temperature exposure during service, diffusion of refractory elements from the superalloy substrate 22 to the NiAl bond coat 24 could take place, thereby potentially degrading the service life of the thermal barrier coating system 20. To avoid this situation and further extend service life, the diffusion barrier layer 32 is additionally beneficial. Suitable processes for forming the barrier layer 32 include carburizing the substrate 22 in accordance with U.S. Patent No. 5,334,263 to Schaeffer, and depositing a layer of AlN or Al-O-N on the substrate 22 by a PVD technique or chemical vapor deposition (CVD).

[0017] According to this invention, the NiAl bond coat 24 is a binary NiAl alloy consisting essentially of nickel and aluminum in stoichiometric amounts and containing zirconium in a very limited amount that has been unexpectedly found to drastically increase the service life of the thermal barrier coating system. In particular, NiAl bond coats containing between about 0.05 and about 0.5 atomic percent zirconium have been shown to drastically improve the life, i.e., increase the spallation resistance, of a thermal barrier coating system.

[0018] During an investigation leading to this invention, specimens of a nickel-base superalloy were provided with thermal barrier coating systems that included a bond coat over which 7% yttria-stabilized zirconia (YSZ) was deposited by EBPVD to a thickness of about 125 micrometers. As indicated in Table I, the bond coats for a first group of superalloy specimens were conventional platinum aluminide (PtAl) diffusion bond coats having a nominal thickness of about 60 to 75 micrometers. Second and third groups of superalloy specimens were coated with a NiAl bond coat containing zirconium at levels of either about 0.05 or about 0.1 atomic percent in accordance with this invention. Each of the NiAl bond coats was deposited by magnetron sputtering to have a thickness of about fifty micrometers. Finally, two groups of cast buttons were formed of NiAl in accordance with this invention to contain zirconium at levels of either about 0.1 or about 0.5 atomic percent. The buttons had a diameter of about one inch (about 25 millimeters) and a thickness of about 0.125 inch (about 3 millimeters). As with the superalloy specimens, the NiAl buttons were also coated with 7% YSZ deposited by EBPVD to a thickness of about 125 micrometers.

[0019] Spallation resistance of the YSZ coats was then evaluated by thermal cycling from room temperature to either about 2075°F (about 1135°C) or about 2150°F (about 1175°C), with a full cycle being completed in about one hour. The results of the test are summarized in Table I.

TABLE I

SPECIMEN	HOURS TO SPALLATION (AVG.)	
	2075°F	2150°F
PtAl Bond Coat	500	180-200
NiAl + 0.05 at.% Zr*	500	(not tested)
NiAl + 0.1 at.% Zr*	1800	(not tested)
NiAl (no Zr additions)**	560-3200+	370
NiAl + 0.1 at.% Zr**	5920+	1620-2000+
NiAl + 0.5 at.% Zr**	1000-2000+	380-760

\* NiAl+Zr coating applied by magnetron sputtering.

\*\* NiAl and NiAl+Zr cast buttons.

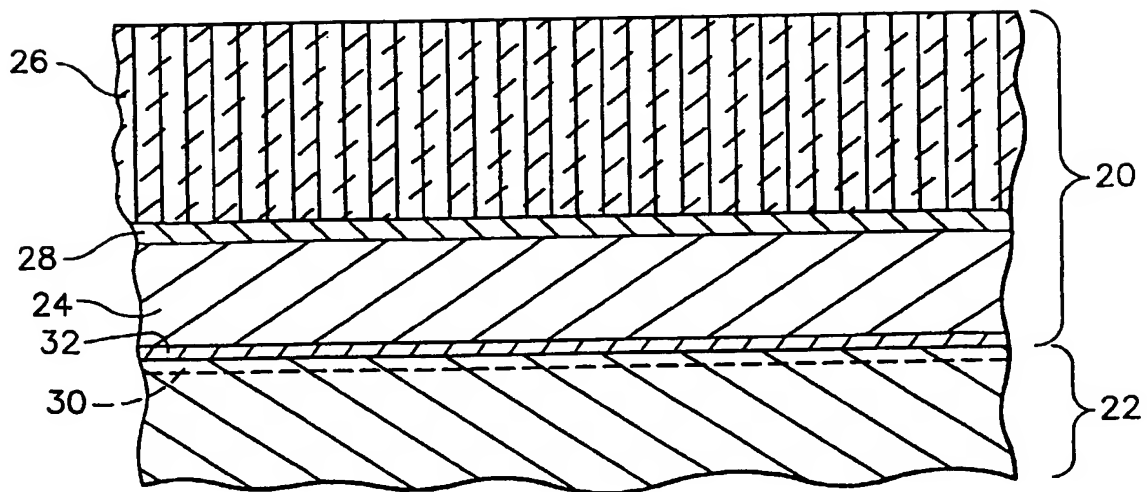
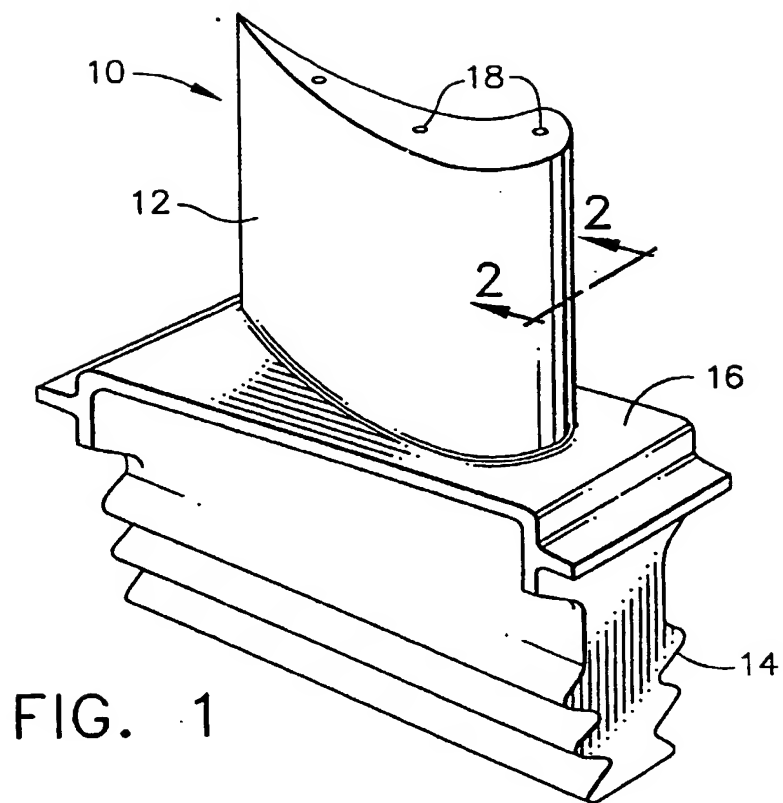
+ Test was discontinued before spallation occurred.

[0020] From the above, it can be seen that the thermal barrier coatings deposited on the NiAl+Zr specimens were considerably more resistant to spallation than those deposited on the conventional diffusion PtAl bond coat. The thermal cycle lives exhibited by the NiAl+Zr specimens containing more than 0.05 atomic percent zirconium were greater by a factor of at least two over the PtAl bond coat specimens at 2075°F and 2150°F. Notably, the improvement in thermal life was unexpectedly good for the specimens whose NiAl bond coats contained 0.1 atomic percent zirconium, particularly at 2150°F where these specimens exhibited an improved thermal cycle life by a factor of ten over the PtAl bond coat specimens. It is believed that improvements in the deposition process employed to form NiAl+Zr bond coats will increase the thermal cycle life of such coatings to that of the button specimens. On this basis, while the above NiAl+0.05Zr bond coat specimens exhibited a thermal cycle life roughly equal to that of the PtAl bond coat, improved deposition techniques will result in NiAl+0.05Zr bond coats having a thermal cycle life between that of the Zr-free NiAl button specimens and the NiAl+0.1Zr button specimens. Finally, it is worth noting that the NiAl+0.5 button specimens exhibited a minimum life of almost twice that of the Zr-free NiAl buttons. Accordingly, while NiAl+0.5Zr bond coats are expected to exhibit improved thermal cycle life over a Zr-free NiAl bond coat, it is apparent that optimum results are obtained with a zirconium content of between 0.05 and 0.5 atomic percent, and likely at or near 0.1 atomic percent. Furthermore, these tests indicated that thermal barrier coating systems equipped with NiAl+Zr bond coats, and particularly the NiAl+0.1Zr bond coat, can be used to considerable advantage in demanding applications where temperatures exceed 2150°F.

[0021] While our invention has been described in terms of a preferred embodiment, it is apparent that other forms could be adopted by one skilled in the art. Accordingly, the scope of our invention is to be limited only by the following claims.

#### Claims

1. A component (10) having a thermal barrier coating system (20) on a surface thereof, the thermal barrier coating system (20) comprising:
  - a bond coat (24) deposited on the surface of the component (10) by a physical vapor deposition technique, the bond coat (24) being a binary NiAl alloy containing about 0.05 to about 0.5 atomic percent zirconium; and
  - a thermal-insulating ceramic layer (26) overlying the bond coat (24).
2. A component (10) as recited in claim 1, wherein the binary NiAl alloy contains nickel and aluminum in stoichiometric amounts.
3. A component (10) as recited in claim 1, wherein the nickel aluminide alloy contains about 0.1 atomic percent zirconium.
4. A component (10) as recited in claim 1, wherein the thermal barrier coating system (20) consists essentially of the bond coat (24), the ceramic layer (26) and an oxide layer (28) therebetween.
5. A component (10) as recited in claim 1, wherein the component (10) is formed of a superalloy.
6. A component (10) as recited in claim 1, further comprising a diffusion zone (30) between the bond coat (24) and the component (10), the diffusion zone (30) having a thickness of up to about five micrometers.
7. A component (10) as recited in claim 1, the thermal barrier coating system (20) further comprising a diffusion barrier layer (32) between the bond coat (24) and the component (10).
8. A component (10) as recited in claim 7, the diffusion barrier layer (32) being selected from the group consisting of a carburized zone in the surface of the component (10), an AlN layer between the bond coat (24) and the component (10), and an Al-O-N layer between the bond coat (24) and the component (10).





European Patent  
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# EUROPEAN SEARCH REPORT

Application Number  
EP 98 30 7244

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	WO 97 29219 A (N.V. INTERTURBINE) 14 August 1997 * page 8, line 14 - line 31 * * page 9, line 12 - line 26 * * page 10, line 1; claims 1-17 *	1-5	C23C28/00
A	US 5 759 640 A (SEETHARAMAIAH MANNAVA) 2 June 1998 * column 4, line 1 - line 15; claims 1,8 *	1,2,4,5	
A	US 5 302 465 A (ROBERT A. MILLER) 12 April 1994		
A	EP 0 471 505 A (JOHNSON MATTHEY PUBLIC) 19 February 1992		
A	PATENT ABSTRACTS OF JAPAN vol. 10, no. 203 (C-360), 16 July 1986 & JP 61 044170 A (TOSHIBA CORP), 3 March 1986 * abstract *		
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			C23C
The present search report has been drawn up for all claims			
Place of search <b>THE HAGUE</b>		Date of completion of the search <b>19 February 1999</b>	Examiner <b>Elsen, D</b>
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			

**ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.**

EP 98 30 7244

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.  
The members are as contained in the European Patent Office EDP file on  
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19-02-1999

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 9729219	A	14-08-1997	US 5824423 A	20-10-1998
			AU 2112897 A	28-08-1997
			EP 0886685 A	30-12-1998
US 5759640	A	02-06-1998	NONE	
US 5302465	A	12-04-1994	NONE	
EP 471505	A	19-02-1992	DE 69122461 D	07-11-1996
			DE 69122461 T	27-02-1997
			JP 5005188 A	14-01-1993